## 4.3 Electrical conductivity of minerals and rocks

- Electronic conduction in metallic minerals and graphite
- <u>Ionic conduction in the pore fluid</u>
- Frequency dependant resistivity, Induced Polarization (IP)

The soils, unconsolidated sediments, and rocks of the crust of the Earth are principally composed of silicate minerals, which are electrical **insulators**. Their resistivities are typically greater than 10<sup>10</sup> Ohm-m and they carry no current. (At high temperature these minerals begin to dissociate and current can be carried by their ions. Resistivity of molten minerals can be less than one Ohm-m.) The current in these materials is carried by ions in the pore solutions.

A subset of minerals, principally metallic sulfides (ore minerals), are electronic semiconductors. A form of carbon, graphite, is a metallic conductor which is found in many crustal rocks.

<u>Figure 4.3.1</u> shows the range of conductivities encountered in crustal minerals and rocks.



# Electronic conduction in metallic minerals and graphite

In metals the charge carriers are electrons that move freely through the metallic crystalline lattice. Relative to rocks and soils the conductivities are very high. The following are typical values for some select metals:

Metals	Resistivity [Ohm-m]
Aluminum	$2.8 \times 10^{-8}$
Copper	1.7 x 10 <sup>-8</sup>
Iron	10 x 10 <sup>-8</sup>
Mercury	95 x 10 <sup>-8</sup>
Silver	1.6 x 10 <sup>-8</sup>
Steel	15-90 x 10 <sup>-8</sup>

Graphite, a form of carbon, is also an electronic conductor, with a resistivity of  $10^{-4}$  to  $5x10^{-3}$  Ohm-m. Graphite occurs in metamorphic rocks and is difficult to distinguish from metallic ore minerals.

Most metallic ore minerals are electronic semiconductors- charge is carried by electrons but by electrons which are normally fixed in the atomic lattice and can be displaced by a field large enough to move them out of a rest position (leaving a 'hole') into an adjacent hole. Their resistivities are lower than those of metals and highly variable because the substitution of impurity ions into the lattice of a particular metallic mineral has a big effect on the resistivity. For example, pure pyrite, FeS<sub>2</sub>, has a resistivity of about  $3x10^{-5}$  Ohm-m but with minor amounts of copper mixed in this can increase to 10 Ohm-m.

The range of resistivity for some typical ore minerals is as follows:

Minerals	Resistivity [Ohm-m]	
Chalcopyrite, CuFeS <sub>2</sub>	$1.2 \times 10^{-5} - 0.3$	
Pyrite, FeS <sub>2</sub>	$3.0 \times 10^{-5} - 1.5$	
Galena, PbS	$3.0 \times 10^{-5} - 3.0 \times 10^{2}$	
Hematite, Fe <sub>2</sub> O <sub>3</sub>	$3.5 \times 10^{-3} - 10^{7}$	
Magnetite, Fe <sub>3</sub> O <sub>4</sub>	$5.0 \times 10^{-4} - 5.0 \times 10^{4}$	



# Ionic conduction in the pore fluids

For most rocks and soils where current is carried by ions in the pore fluid the resistivity depends on the following rock properties:

Porosity (intergranular and fracture)

Pore fluid resistivity (salinity)

**Temperature** 

The Computation of Bulk resistivity as a function of porosity, pore

<u>fluid salinity and temperature</u>

Pore fluid saturation

Clay content

<u>Pressure</u>



# Porosity (intergranular and fracture)

In most rocks there is an empirical relationship, established by G. E. Archie (1942), between the ratio of the bulk rock resistivity,  $\rho_b$ , to the pore fluid resistivity,  $\rho_f$ , called the formation factor, F, and the volume fraction porosity,  $\varphi$ . The relationship, now called Archie's law, is:

$$\frac{\rho_b}{\rho_f} = F = a \phi^{-m}$$

Alternatively,  $\rho_b = \rho_f a \phi^{-m}$ .

For the typical sandstones of oil reservoirs Archie found that the coefficient **a** was close to one and the exponent m was close to two. Subsequent work with other rocks and even unconsolidated sediments shows that this power law is generally valid but with varying coefficients and exponents. The following table by Keller (1996, Table 10) summarizes the coefficients for different materials.

Rock	φ	a	m
Weakly cemented, detrital (Tertiary)	0.25 - 0.45	0.88	1.37
Moderately well cemented (Mesozoic)	0.22 - 0.35	0.62	1.72
Well cemented (Paleozoic)	0.05 - 0.25	0.62	1.95
Dense, igneous, metamorphic	< 0.05	1.4	1.6
High porosity volcanic	0.2 - 0.8	3.5	1.4

Archie's Law readily explains the wide range of observed rock resistivities (Figure 4.3.2). Reasonable ranges for porosity and pore fluid resistivity yield a range of bulk rock resistivities of almost **five orders of magnitude**.

Archie actually began his work hoping to find a relationship between permeability and resistivity. Figure 4.3.3 is a page from one of his early papers showing resistivity vs. both permeability and porosity. Unfortunately permeability is a very weak function of resistivity and no useful relation has ever emerged. At the root of this problem is the fact that

there is usually no strong correlation between porosity and permeability, as seen in <u>Figure 4.3.4</u>. Further, on the microscopic scale conductance is controlled by the square of the radius (area) of the cross sectional area of the pore passages through the rock while permeability depends on a higher power of the radius of these passages.

[Consider current flow through a capillary tube of radius r and length L under an applied voltage V. The current is given by:

$$I = \frac{V}{R} = \frac{\pi r^2 V}{\rho L} = \frac{\pi r^2 E}{\rho} = -\frac{\pi r^2}{\rho} \cdot \nabla \phi$$

where the electric field E, V/L, has been expressed as the gradient of the potential.

Darcy's Law for volumetric fluid flow rate  $q_f$  under an hydraulic gradient  $\nabla P$  is:

$$q_f = k_h A \nabla P = k_h \pi r^2 \nabla P$$

where A is the cross sectional area normal to the flow direction and  $k_h$  is the hydraulic conductivity.

To derive values for  $k_h$  in rocks made up of small pore passages or tubes, Poiseuille's Law for flow through a capillary tube of radius r is invoked:

$$q_f = \frac{1}{8\mu} r^2 \cdot \pi r^2 \nabla P.$$

It is seen that for capillary flow the hydraulic conductivity itself is proportional to the square of the radius of the pore passage and so the overall flow varies with the fourth power of the radius.]

Finally it must be noted that Archie worked with rocks saturated with low resistivity brines typical of the oil field environment. For such rocks it is observed that for a given porosity the formation factor is constant as the resistivity of the pore fluid is changed. However as the pore fluid resistivity increases, as the water becomes fresher, it is found that the formation factor begins to decrease. This implies that another mechanism is involved in conduction that provides a path for current flow as the main pore space path becomes resistive. Caution must be used in applying Archie's law for fresh water sediments because the resistivity may be dominated by this alternate path. We will return to this topic below in the discussion of the role of clay in determining resistivity.

The porosity discussed so far has been the intergranular porosity encountered in most sedimentary rocks. Fracture porosity is equally important for resistivity since the planes of parallel fractures are essentially short circuits or fast paths for current conduction. The plot of Figure 4.3.5 shows the ratio of conductivity parallel to the bedding planes (the longitudinal conductivity) to the host rock conductivity as a function of the volume fraction of fracture porosity and the rock porosity. In this figure the host rock conductivity is calculated using an Archie m coefficient of 2. The rock porosities are given with each curve. It has been assumed that the fluid in the rock is the same as that in the fractures. The conductivity perpendicular to the bedding plane, the transverse conductivity, is unaffected by small fracture porosity and so the vertical axis can be interpreted as the coefficient of anisotropy. It is clear that small fracture porosity can have an enormous effect on anisotropy. For example in a rock of 0.1 porosity and 0.01 fracture porosity, the anisotropy is a factor of two.

Such bedding plane anisotropy can also be achieved by both macroscopic and microscopic layering of minerals (clays) or rock units (sand-shale sequences). The model of <u>Figure 4.3.5</u> can be modified for these situations and anisotropies of 2 to 3 are easily found and match field observations.



# Pore fluid resistivity (salinity)

A plot of pore fluid conductivity vs. salinity (concentration) for a variety of electrolytes is given in <u>Figure 4.3.6</u> (from Keller, 1996). The values for most formation fluids cluster around the NaCl curve. For reference Berkeley tap water is about 100 Ohm·m with a salinity of about 40 ppm (one of the purest public water supplies in the nation) and sea water is about 0.3 Ohm·m with a salinity of 30,000 ppm.



## **Temperature**

The resistivity of the pore fluid decreases with increasing temperature because the mobility of the ions in solution increases with temperature. This property of solutions is the opposite of the behavior of metallic (electronic) conductors where the resistivity increases with temperature. An approximate formula for the resistivity as a function of temperature is:

$$\rho_f(t) = \frac{\rho_{18^{\circ}C}}{1 + \alpha(t - 18)}$$
 where  $\alpha \approx 0.025$ 

The plot of resistivity vs. temperature for a NaCl solution, <u>Figure 4.3.7</u>, is representative of a wide range of solutions and may be substituted in Archie's Law to determine the change in bulk rock resistivity with temperature.



# The Computation of Bulk resistivity as a function of porosity, pore fluid salinity and temperature

An algorithm for computing the bulk resistivity based on Archie's law and the above formulas for pore fluid resistivity for various temperatures and concentrations is provided in interactive Figure 4.3.8. The calculations are based on an NaCl solution. The coefficients of Archie's law as well as the relevant porosity, temperature, and concentration (or the desired ranges of these parameters) are the model parameters and the graphs are of bulk resistivity vs. porosity, temperature or concentration.

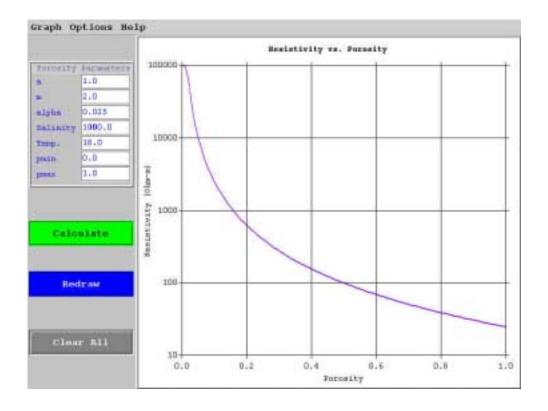


Figure 4.3.8



## Pore fluid saturation

The saturation, S, is the fraction of the pore space that is actually filled with fluid. For brine filled sandstones another power law relationship, also attributed to Archie, appears to hold:

$$\rho_b = \rho_{b \ 100} \ S_w^{-2}$$

where  $\rho_{b\ 100}$  is the rock resistivity at 100% saturation and  $S_w$  is the water saturation.

This relation holds for saturations above the **critical saturation**,  $S_c$ . The critical saturation occurs at that point in draining a sample where further removal of fluid drains the pore passages linking the larger pore 'reservoirs' shown in <u>Figure 4.3.9</u>. Once these connectors are broken the resistivity grows very rapidly with the exponent of  $S_w$  reaching as high as 4. With complete draining there still remains some fluid either trapped in closed

pores or bound to the mineral surfaces. This is referred to as the irreducible saturation and so all rocks have an upper bound on their low saturation resistivity set by the irreducible saturation. <u>Figure 4.3.10</u> is a schematic plot of resistivity (and seismic velocity) vs. water saturation.



#### Clay content

The presence of clay lowers the bulk resistivity of soil or rock and causes the resistivity to become frequency dependant. We will first consider the reasons that cause the resistivity to be reduced. The effect on the bulk resistivity was first noticed in studies of rocks containing clay where it was found that the Archie equation obtained with low resistivity pore fluids consistently overestimated the bulk resistivity predicted when high resistivity pore fluids were substituted. The effect is due to the fact that clay minerals have an electrically 'active' surface layer. This active surface not only affects the electrical resistivity of clay water mixtures but it also affects the degree to which water is held within the clay structure and so ultimately influences the mechanical strength and density of soils containing clay. The latter properties are beyond the scope of this course and are very well described in a classic text by Mitchell (1993). To better understand the role of clay in influencing the electrical resistivity we need to review some basic clay properties. The following summary is taken from Mitchell.

The basic structure of a typical clay particle consists of alternating layers of two sheet-like crystalline lattices. The first is a planar structure of silica tetrahedra, silicon atoms surrounded by oxygen atoms on the vertices of an enclosing tetrahedra. The second is a planar structure of octahedral units consisting of either magnesium or aluminum atoms surrounded by hydroxyls or oxygen atoms on the vertices of the enclosing octahedra. The typical clay mineral is a sandwich consisting of one sheet of the octahedral lattice between two tetrahedral sheets.

At the time of formation other ions can be substituted for the basic silicon, magnesium or aluminum in the lattice. In the tetrahedral layer aluminum can replace silicon and in the octahedral layer magnesium replaces aluminum or iron replaces magnesium. If the original or ideal structure was electrically neutral then substituting Mg<sup>++</sup> for Al<sup>+++</sup> leaves a

net negative charge. To maintain electrical neutrality the clay particle attracts cations to its surface from its surroundings. These cations are not part of the crystalline structure of the clay, they are simply drawn from the aqueous solution that surrounds the clay at its formation. They may be replaced by other ions when the clay formation evolves and the aqueous environment changes. They are said to be exchangeable and the quantity that is available for exchange, which in turn depends on the number of negative charges present in the actual clay lattice, is called the Cation Exchange Capacity (CEC). Ions held adjacent to the exposed lattice structure of the surface can be released into solution and ions in the solution can be drawn to sites on the surface. Clays can thus take ions from the solution and replace them with different ions from their structure.

An important net effect is that when water is added to clay the concentration of ions is increased in the solution in the vicinity of the clay surface. While some of these released ions and polar water molecules held tightly to the surface, the fixed layer (or Stern layer), others are held less strongly in a diffuse but mobile layer extending into the solution. These ions diffuse into solution as a result of the concentration gradient but are also held by the voltage gradient (the electric field) of the negatively charged clay surface. The charged surface and its associated zone of decreasing ion concentration is called the diffuse double layer. 4.3.11 is a schematic picture of the ion concentration and the potential distribution away from the surface. This diffuse layer has a higher conductivity than the normal pore fluid and represents a parallel low resistivity path for current conduction along the mineral surfaces. Clay particles have an enormous surface area per unit weight and consequently a relatively small amount of clay can dramatically increase the bulk conductivity. The effect is most dramatic when the pore fluid is of high resistivity and is insignificant for highly concentrated pore fluids, which carry the current easily without the benefit of the surface conduction paths.

Waxman and Smits (1968) derived relatively simple expression that specifically ties the apparent formation factor  $F_a$  to the true formation factor F (the formation factor measured at high pore solution concentration) and the cation exchange capacity via:

$$F_{a} = \frac{\rho_{b}}{\rho_{w}} = \frac{F}{1 + \rho_{w}BQ}$$

where Q is the cation exchange capacity per unit volume of the clay and B is a factor which accounts for the variation of the ion mobility with solution concentration.



#### Pressure

The role of pressure, at least confining pressure, is to increase the bulk resistivity of a rock. The effect is caused by the decrease in pore volume as the rock is compressed. A simple relationship between the change in resistivity and the strain may be derived directly from Archie's Law provided the strain is accommodated by the change in pore volume. If we take the derivative of the bulk resistivity with respect to porosity (a very big if since it is not really clear if Archie's Law works for stress induced changes in volume) we obtain:

$$\frac{\Delta \rho_b}{\rho_b} = -m \frac{\Delta \phi}{\phi} = -m \frac{\varepsilon}{\phi}$$

where  $\varepsilon$  is the volumetric strain. The strain is amplified first by the inverse of porosity and also by the exponent  $\mathbf{m}$  in Archie's Law. So for a porosity of 0.01 and an exponent of 2 the fractional change in resistivity is 200 times the strain. Thus we see that resistivity may be a very sensitive monitor for strain especially in low porosity materials. It has been presumed in this analysis that the rock is permeable and that the fluid is squeezed out as the porosity is reduced. (If it is not the pore pressure can increase above hydrostatic and the formation is said to be overpressured. Under these conditions increased pore pressure may actually increase the effective porosity and the resistivity will decrease.)

A laboratory measurement of the effect confining pressure on the resistivity of low porosity granite is shown in <u>Figure 4.3.12</u>. The pressure effect can be dramatic in fractured rock where the fractures normal to the principle stress close while others remain open. This brings about a significant change in the anisotropy of the rock.



#### Frequency Dependent Resistivity, Induced Polarization (IP)

IP in rocks containing metallic minerals
IP in rocks and soils containing clay

It is observed in field and laboratory measurements that the resistivity or the apparent resistivity is a function of the frequency of the applied current. The effects are observed over a range of frequencies from 10<sup>-4</sup> Hz to 10<sup>4</sup> and higher. It was also observed in early field measurements employing a switched DC current, that the voltage across the measuring electrodes decayed slowly after the current was shut off. These effects are particularly pronounced in rocks containing metallic ore minerals and in rocks or soils containing clay.

Because the resistivity is frequency dependant we have seen that it must be complex: the measured voltage has a component in phase with the current and a component 90 degrees out of phase (in quadrature) with the current. The real and imaginary components of V/I (proportional to the resistivity) have the following form:

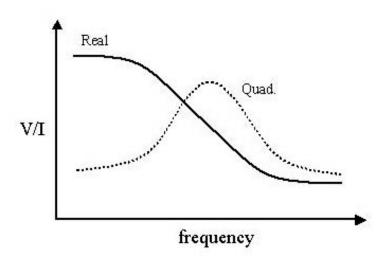


Figure 4.3.13

The important observation is that the amplitude of the resistivity decreases with increasing frequency and the imaginary component has a maximum at a frequency known as the relaxation frequency. The frequency band over which the maximum change in resistivity occurs and where the imaginary

component maximizes is known as the dispersive region. (Formally any quantity that changes with frequency is said to be dispersive).

The time transient of the voltage across the sample or between the field electrodes when the current is shut off has the following form:

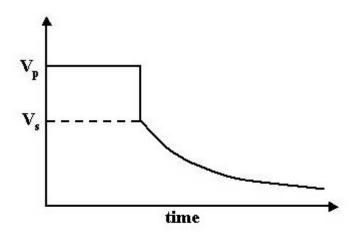
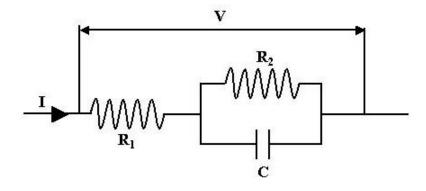


Figure 4.3.14

The voltage has a characteristic step drop followed by an exponential-like decay with a time constant ranging from milliseconds to tens of seconds. In the IP literature the ratio of  $V_s/V_p$  is known as the chargeability,  $\mathbf{m}$ .

The voltage decay after the current is shut off suggests an energy storage mechanism in the material. Qualitatively the transient and frequency domain observations for the resistivity are compatible with the response of the resistor-capacitor circuit analog shown in Figure 4.3.15.



#### Figure 4.3.15

At DC the capacitor is an open circuit and all the current passes through the sum of  $R_1$  and  $R_2$ , developing a voltage  $V_p = I (R_1 + R_2)$ . As the frequency increases, current can flow through the capacitor, which decreases the overall resistance. Finally at high frequency the current is effectively short circuited by the capacitor and the voltage developed is simply I  $R_1$ . Between the DC and high frequency limits the voltage across the capacitor is phase shifted 90° from the current and so adds an imaginary component to the total voltage measured across the circuit, which peaks midway between the low and high frequency asymptotes. Thus we see that this circuit faithfully reproduces the key features observed in measurements.

In the time domain this qualitative explanation is equally satisfying. At DC, before the current is switched off, the capacitor is charged to the voltage across  $R_2$ , i.e.  $IR_2$  (= $V_s$ ). When the current is shut off the voltage drop across  $R_1$  disappears immediately and the capacitor begins to discharge through  $R_2$  from its initial voltage  $V_s$ . The total voltage across the circuit  $V_p$  thus drops initially to  $V_s$  and then decays exponentially with the time constant  $R_2$ C. At the instant of shutoff:

$$V_s/V_p = R_2/(R_1 + R_2) = m$$

There is a danger in pursuing the simple circuit analog too far in attempting to explain the macroscopic behavior of a rock sample or of the ground. Nevertheless the circuit representation is useful because it focuses inquiry on what sort of mechanisms might exist to provide capacitive-like energy storage in rocks containing metallic minerals or clay. Capacitance is basically a charge separation phenomenon and so we need to look for mechanisms that would permit ionic separation under the application of an electric field. It is tempting to invoke the polarization concept but it was developed for bound charge and the phenomenon here has to do with free charges, ions, that move through the fluid.

A variety of terms have been used for this phenomenon in the geophysical literature. Complex resistivity and spectral resistivity were introduced to emphasize the frequency dependence but the most common term is induced polarization, IP, which was used because the underlying microscopic cause of the effect is a charge separation (a polarization)

induced by the application of an electric field. We will first consider the IP effect in rocks containing metallic minerals and then for rocks and soils containing clays.



# IP in rocks containing metallic minerals

A simple model used to describe current flow in a rock containing a distribution of metallic minerals is that shown in Figure 4.3.16. In a pore passage that is blocked by a metallic mineral the current must cross the interface from the pore fluid, where current is carried by ions, to the metallic mineral where the current is carried by electrons. This is a classic problem in electrochemistry and there is an extensive literature dating from Michael Faraday on the physics and chemistry of this interface and of the chemical reactions that occur in transferring charge across it. The interface itself is similar in some respects to that of a clay particle. The metallic lattice also presents a net negative charge to the adjoining solution and it consequently draws cations and polar water molecule into a tightly bound fixed or surface layer on the mineral surface. The problem is further complicated however because the metallic mineral, unlike the clay mineral, can actually release ions from the lattice into solution providing additional cations in the diffuse layer. This is actually the mechanism of corrosion wherein ions of a metal continuously dissolve into solution. Whether corrosion occurs or not depends on the voltage that exists between the metal or metallic mineral and the adjacent solution. A current can flow as ions leave the surface. If an added voltage is applied across the interface, the overvoltage in electrochemical parlance, the net current flow can either be increased (more ions brought into solution) or decreased depending on the polarity of the applied voltage. (The latter is the basis of cathodic protection used to halt corrosion of metals). Other reactive ions in the solution may be brought to the interface and react with the metallic ions in the mineral or simply take It is these fundamental charge transfer electrons from the surface. mechanisms that provide a means for current to be carried across the interface when a small alternating voltage is applied.

Each such reaction uses a small amount of energy which from an electrical point of view looks like ohmic dissipation or I<sup>2</sup>R loss. In an equivalent circuit representation of the interface these charge transfer reactions have an equivalent resistance called the reaction resistance or polarization resistance.

The diffuse double layer itself is also a capacitor. The fixed surface of negative charge and the adjacent diffuse layer of cations have a well defined charge and effective charge separation, d, and with an appropriate selection of the effective dielectric constant  $\kappa$ , the capacitance per unit surface area is defined as  $\kappa\epsilon_0/d$ . The capacitance is usually broken down into the fixed layer capacitance due to the combination of the metallic surface and the Stern layer and the diffuse layer capacitance due to the mobile layer beyond the Stern layer. This series combination of capacitors is called the double layer capacitance.

When an alternating voltage is applied the interface can be represented by the following equivalent circuit:

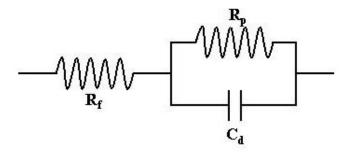


Figure 4.3.17

Where  $R_p$  is the reaction resistance,  $C_d$  is the double layer capacitance, and  $R_f$  is the resistance of the pore fluid leading up to the interface. The actual movement of ions to and from the interface reaction is controlled by diffusion which in a detailed analysis reveals that the effective reaction resistance is itself frequency dependent and thus complex. The impedance presented by a diffusion controlled process is called the Warburg impedance,  $Z_W$ , and it has the form:

$$Z_{W} = \frac{X_{W}}{\sqrt{i\omega}}$$

The metallic mineral resistance is in series with the pore fluid resistance and the interface resistances. A similar interface impedance is encountered as the current leaves the metallic particle but the net effect of the particle blockage is accounted for with one equivalent circuit.

In an actual rock there would presumably be some parallel pore paths that were not blocked by metallic minerals and so a schematic of the complete equivalent circuit would be that shown below.

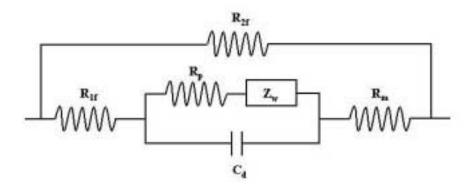


Figure 4.3.18

It is important to note that the interface impedance acts like a gate or valve for the current. Both  $Z_W$  and the impedance of  $C (= 1/\omega C)$  become large at low frequency and so the path through the metallic mineral grain is blocked. At high frequency the interface impedance drops, which not only opens a parallel path but opens one that is much lower resistance than a normal fluid filled pore path.

This final circuit, that we have derived from a microscopic model of the interface, has the arrangement of resistive and capacitive elements that were called for in the explanation of the observed frequency and time domain measurements. This model, with many modifications to accurately reflect some of the more subtle features of the electrochemical reactions at the interface has been remarkably successful in characterizing the IP response of rocks containing metallic minerals. It has not been particularly successful for identifying the actual metallic mineral involved, probably because the bulk effect depends on the actual reactive ion species, the particle size and distribution as well as the composition of the metallic mineral. It should also be remembered that none of the metallic sulfide minerals are found in a pure form: they invariably contain other metals in their crystalline structure and these may influence the reaction resistance as well as the properties of the double layer.



## IP in rocks and soils containing clay

The mechanism for charge storage when clay is present depends on the fact that the mobility of anions and cations is different in the diffuse layer adjacent to the clay surface than in the pore fluid in a clay free zone. The current in this zone is carried predominantly by cations because they predominate. This lowers the effective mobility of the anions and the net result is a selective transference of anions in the clay rich zone. The actual transference number, the fraction of current carried by the particular ion, depends on the relative concentration of cations in the clay rich pores compared to their concentration in the normal solution. This in turn depends on the CEC and the pore fluid concentration. In well ordered clays with high CEC such as montmorillonite it is not uncommon to have cation transference numbers above 0.9. This zone selectivity, with its accompanying polarization when an external field is applied, is usually referred to as membrane polarization. In a simple model, the soil or rock is made up of alternating zones of clay-rich and clay-free pores. Because the mobilities are different in these zones, when a field is applied ions will accumulate at the interfaces between zones and this provides the capacitive element in the equivalent circuit. Some ions do flow through the interface albeit with a higher resistance to flow than in the clay free pores and there are alternate parallel paths just as there are in the model in which metallic particles block the pore paths. A schematic model of these alternating zones, taken from Fraser (1964) is shown in Figure 4.3.19. In detail the actual movement of ions to and from the interface is controlled by diffusion and is represented by a Warburg impedance.

The impedance of the resulting composite of zones has both the ordinary capacitance and the diffusion controlled term as well as the series and parallel resistive terms.